

MINERALOGY OF PERMEABLE REACTIVE BARRIERS FOR THE ATTENUATION OF SUBSURFACE CONTAMINANTS

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ABSTRACT

Permeable reactive barriers (PRBs) are a relatively recent development of a passive system to remediate subsurface waters containing organic or inorganic contaminants. Groundwater flow under a natural gradient passes through a permeable curtain of treatment medium that either precipitates the contaminants as relatively insoluble compounds or transforms the contaminants into environmentally acceptable or benign species. The most widely adopted treatment medium is submillimetric zero-valent iron, a substance that is highly reactive, environmentally acceptable, and is readily available as a manufactured product derived from the recycling of scrap iron and steel. Organic compost wastes have also been used to ameliorate inorganic contaminants, and two case studies of the utilization of composts to reduce sulfate and precipitate metals are presented, primarily from a mineralogical perspective. In cores of the reacted treatment media, the most abundant secondary product formed *in situ* is Fe oxyhydroxide, but a variety of precipitates has been identified. For example, secondary pyrite, greigite, and native nickel are present at a site at which replacement of organic material by sulfides is common. At an industrial site, secondary pyrite, covellite, chalcopyrite, and bornite have formed in the treatment medium, and whereas replacement of organic material by Fe oxyhydroxides is widespread, replacement by sulfides is rare. The secondary sulfides and metals are volumetrically small and are unlikely to impede the permeability of the treatment medium, but the formation of Fe oxyhydroxides and secondary carbonates in the presence of zero-valent iron requires further monitoring to determine whether the secondary precipitates and the consumption of Fe⁰ will appreciably lessen the effectiveness of such PRBs over the long term. Current indications are that PRBs are both an environmentally effective and a cost-effective technique of remediation.

Keywords: permeable reactive barriers, metals contamination, organic treatment media, sulfate reduction, Fe oxyhydroxides, secondary sulfide precipitates, zero-valent iron, Nickel Rim, Canada.

SOMMAIRE

L'installation de barrières réactives perméables est un développement assez récent pour dépolluer les eaux souterraines contaminées par des produits organiques ou inorganiques. L'écoulement souterrain suit un gradient naturel qui passe au travers d'un rideau perméable contenant un médium traitant qui soit précipite les contaminants sous forme relativement insoluble, ou bien les transforme en espèces acceptables ou bénignes pour l'environnement. Le traitement le plus répandu utilise le fer métallique submillimétrique, substance très réactive, acceptable pour l'environnement, et facilement disponible comme produit du recyclage de ferraille et d'acier. On se sert aussi des déchets de composts organiques afin d'éliminer les contaminants inorganiques. Nous présentons à titre d'exemples deux cas d'utilisation de composts pour réduire la teneur en sulfate et pour précipiter les métaux présents, surtout d'une perspective minéralogique. Dans les carottes du médium de traitement ayant servi, le produit secondaire le plus abondant formé *in situ* serait un oxyhydroxyde de fer, mais divers précipités ont été identifiés. Par exemple, les phases secondaires pyrite, greigite, et nickel natif sont présentes au site où il y a remplacement de matériaux organiques par des sulfures. A un site industriel, la pyrite, covellite, chalcopyrite, et bornite secondaires se sont formés dans le médium de traitement. Tandis que le remplacement de matériaux organiques par des oxyhydroxydes de fer est répandu, un remplacement par des sulfures semble rare. Les sulfures secondaires n'occupent qu'un petit volume, et sont peu propices à réduire la perméabilité du médium de traitement, mais la formation des oxyhydroxydes de fer et des carbonates secondaires en présence de fer métallique

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requiert une surveillance continue afin de déterminer si les précipités secondaires et la consommation du Fe^0 diminuent de façon importante l'efficacité de telles barrières à long terme. Il semble clair, d'après les indications actuelles, que ces barrières sont environnementalement efficaces et rentables.

(Traduit par la Rédaction)

Mots-clés: barrières réactives perméables, contamination par métaux, médium de traitement organique, réduction de sulfate, oxyhydroxydes de fer, précipités de sulfures secondaires, fer natif, Nickel Rim, Canada.

INTRODUCTION

A significant advance in remediation technology that has been developed over the past decade to attenuate high aqueous concentrations of environmentally detrimental substances, both organic and inorganic, is the permeable reactive barrier or PRB (Blowes *et al.* 1995a, b, 2000, Naftz *et al.* 2002, Richardson & Nickelow 2002). PRBs, also commonly referred to as treatment walls or permeable reactive walls, are usable to ameliorate contaminants in subsurface groundwater; the demonstrated effectiveness of PRBs has resulted in a substantial recent increase in the number of full-scale and pilot-scale units that have been installed. The total number of full-scale installations at present is small, but most PRBs have been constructed only within the past few years; for example, although the first full-scale commercial application of a PRB, which was emplaced to remediate chlorinated solvents, was in February 1995 at Sunnyvale, California (Warner *et al.* 1998), a recent estimate is that there may be as many as 200 PRBs currently operating (ITRC 2005). Applications of PRB technology will likely continue to increase, especially when the technology is more widely adopted in Europe.

Here we describe the case histories of two PRBs: one treats acid mine-drainage (AMD), and the other treats heavy metals at an industrial site. The barrier at the AMD site relies on organic carbon as a medium for contaminant attenuation, whereas both organic carbon and Fe^0 are used in various parts of the treatment wall at the industrial site.

BACKGROUND INFORMATION

Subsurface groundwater contaminants are commonly remediated by a pump-and-treat system in which the contaminant plume is intercepted by boreholes, and the groundwater is brought to the surface for treatment. PRBs have the advantage of being a passive system that, once installed, requires no maintenance or ongoing expenditures beyond those of optional monitoring, and requires no surface infrastructure. PRBs are also viewed favorably because they are able to treat an extremely wide variety of contaminants. About three-quarters of the full-scale installations are designed to remediate organic contaminants, predominantly chlorinated solvents such as trichloroethylene, tetrachloroethylene,

and carbon tetrachloride. In Figure 1, we provide an indication of the most common inorganic contaminants that are treated, and in Table 1, list only a few of the tested elements and a few of the numerous pertinent references that are available.

About three-quarters of the current full-scale PRBs use iron metal as the reactant medium. Other metals, such as Zn, Mg, and Sn, have proved effective in laboratory tests (Boronina *et al.* 1995, 1998, Warren *et al.* 1995), and applications of many of the host of other tested reactive media, such as zeolites, Fe oxyhydroxides, and organic compounds, are given by Scherer *et al.* (2000) and Vidic & Pohland (2000). The advantage of zero-valent iron is that, in addition to being effective, it is inexpensive and readily available in bulk quantities, and unlike many other metals, it is non-toxic. The iron, commonly referred to as "iron filings" or "granulated iron", is commercially available and produced from scrap iron and steel. It typically is impure. In the manufacturing process, the filings are heated at 700

TABLE 1. SELECTED EXAMPLES AND REFERENCES TO PRB APPLICATIONS

Substance	Comments	Selected references
chromate	$\text{Cr}^{6+} \rightarrow \text{Cr}^{3+}$ uptake as $(\text{Fe}, \text{Cr})\text{OOH}$ has been demonstrated	Powell <i>et al.</i> (1995), Blowes <i>et al.</i> (1997, 1999), Pratt <i>et al.</i> (1997), Astrup <i>et al.</i> (2000)
uranium	$\text{U}^{6+} \rightarrow \text{U}^{4+}$ possibly $\text{UO}_2 \rightarrow \text{UO}_2 \cdot n\text{H}_2\text{O}$ or by sorption; uptake by sorption rather than by reduction concluded by Qui <i>et al.</i> (2000)	Gu <i>et al.</i> (1998, 2002), Fiedor <i>et al.</i> (1998), Naftz <i>et al.</i> (2000), Morrison <i>et al.</i> (2001), Matheson <i>et al.</i> (2002)
arsenic	$\text{As}^{5+} \rightarrow \text{As}^{3+}$ objective is sorption, <i>e.g.</i> , to Fe oxyhydroxides because As^{3+} is ~60 times more toxic than As^{5+}	McRae <i>et al.</i> (1999), Manning <i>et al.</i> (2002), Melitas <i>et al.</i> (2002a, b), Bain <i>et al.</i> (2003), Su & Puls (2003)
AMD*	typically high sulfate; various metals and semimetals	Benner <i>et al.</i> (1997, 1999), Blowes <i>et al.</i> (1995b), Shokes & Müller (1999)
multi- element	Se, Cr, U U, Mo, Tc, Cr U, Mo, As, Se, V, NO_3	Qui <i>et al.</i> (2000), Cantrell <i>et al.</i> (1995), Morrison <i>et al.</i> (2002)

* AMD: acid mine-drainage.

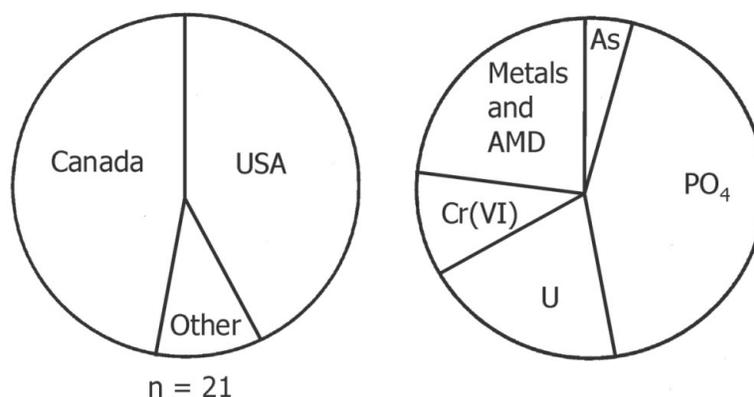


FIG. 1. Early distribution of full-scale PRBs and their applications (data from Smyth *et al.* 2002).

to 1200°C in rotary kilns to burn off the non-metallic materials, especially the cutting oils (Ritter *et al.* 2002). The heating stage promotes oxidation, and the final product generally has a “rusty” appearance because of the presence of surficial iron oxides. Particle sizes of the Fe⁰ from various producers are typically submillimetric (Johnson *et al.* 1996).

GENERAL PRINCIPLES

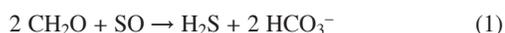
A PRB consists of a zone or curtain of permeable reactive material that is placed in the flowpath of contaminated groundwater so that, during passage through the curtain under a natural gradient, reaction between the contaminants and the emplaced material improves the quality of the aqueous outflow. Because the design is for flow under a natural gradient, the system is categorized as “passive” rather than “active”; the latter, such as a pump-and-treat system, requires a continued input of energy to maintain the remediation process. The ideal physical setting for a PRB is one in which the contaminant plume is near surface, is laterally of limited dimension, and is underlain by bedrock or a similarly effective aquitard. These conditions serve to direct the contaminant plume to a focal point at which the PRB can be conveniently installed to intercept the plume. In less favorable circumstances, however, impediments to lateral flow can be constructed to funnel the contaminant plume toward an interception point. Arrangements of this type are commonly referred to as funnel-and-gate systems. Various funneling systems, which may consist simply of interlocked, corrugated steel sheets driven vertically into the ground, have been described by Gavaskar *et al.* (1998).

The within-barrier reactions depend on the geochemical nature of the inflow and the composition of the reactive medium. The emphasis here is on inorganic

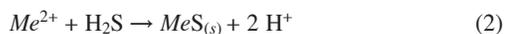
subsurface contaminants, but PRB methodology is equally applicable to the treatment of surficial organic and inorganic seepages; the technology, for example, has been investigated for remediation of drainage from acid sulfate soils (Waite *et al.* 2002). Removal of contaminants by PRBs involves two main processes (Scherer *et al.* 2000): (1) transformation, whereby the contaminant undergoes a change to a less harmful compound, and (2) immobilization, whereby the contaminant is retained within the barrier either by sorption to the reactive medium or by precipitation of the dissolved phase. The transformation mechanism applies mainly to organic materials, such as chlorinated compounds, that are transformed to less harmful or to benign species. Immobilization within a barrier is the principal mechanism that operates for dissolved inorganic contaminants. Nevertheless, the exact nature of the immobilization, whether by precipitation of the deleterious species or by sorption to either the barrier’s original materials or to newly formed compounds, is not yet understood well because few mineralogical examinations have been done on functioning field-scale PRBs, most of which have been installed relatively recently. Determination of the mineral–solution reactions that occur is important because the results not only provide indications of the stability of the products that are formed, but they will also aid future design in terms of the reactive mixtures employed. In the two case studies presented here, the mineralogical data suggest that precipitation is the principal attenuating mechanism, and that sorption is associated with newly formed products, chiefly Fe oxyhydroxides, rather than with the initially emplaced reactive medium.

Although sulfate-reducing bacteria have been shown to be active where zero-valent iron is the treatment medium (Rowland 2002), both of the case-study PRBs use organic matter as a means of inducing reductive

biotransformation (Benner *et al.* 1998, 1999). The organic matter provides both a nutrient source for bacteria and a high capacity to deplete dissolved oxygen. Maintenance of anoxic conditions is most readily attained in subaqueous domains because dissolved oxygen has a relatively low solubility in water. At sufficiently low Eh, dissolved metals such as Fe^{2+} and Cu^+ can be precipitated as native metals. Under acidic conditions, the reaction for the reduction of dissolved sulfate can be written as



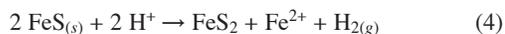
where CH_2O is a generic term for simple organic carbon compounds. In the presence of dissolved metals (Me):



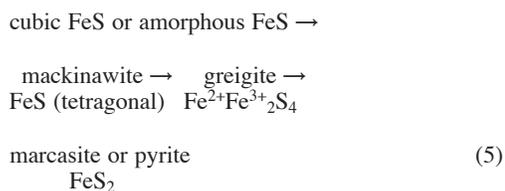
which for Fe^{2+} corresponds to



Reaction (3) is considered to dominate at acid pH and $S = <10^{-3} M$, and becomes more important at temperatures $<25^\circ\text{C}$ (Rickard *et al.* 1995). The formation of Fe disulfide proceeds through loss of Fe from the monosulfide (Wilkin & Barnes 1996, Benning *et al.* 2000):



Although various other sequences have been observed (*e.g.*, Wikjord *et al.* 1980, Shoesmith *et al.* 1980), it is generally accepted that formation of FeS_2 proceeds via the following pathway (Rickard *et al.* 1995, Lennie & Vaughan 1996), wherein amorphous FeS has recently been determined to be disordered mackinawite (Wolthers *et al.* 2003, 2005):



Systems containing organic carbon are chiefly concerned with treatment of heavy metals rather than sulfate, but generation of hydrogen sulfide through the action of sulfate-reducing bacteria has the beneficial effect of immobilizing metals as sulfides that have low solubilities and are likely to remain stable even under variable conditions. Reaction (1) has the beneficial effect of adding alkalinity to the system, and although the large number of species referred to as sulfate-reducing bacteria can operate effectively even at $\text{pH} \leq 3$ (Koschorreck *et al.* 2003), the bacteria generally have optimal growth approximately in the pH range 6

to 7. Thus, for treatment of the effluents related to acid mine-drainage, addition of pH-raising material, such as a small amount of limestone, to the reactive medium provides a means of optimizing conditions of growth during the initial period of microbial growth.

Previous mineralogical studies

The solid-phase products formed during reactions with PRB treatment media for the precipitation of dissolved metals have been examined either in numerous laboratory-scale experiments, especially those involving zero-valent iron in the medium, or the mineral precipitates have been inferred on the basis of geochemical modeling (Amrhein *et al.* 1998, Odziemkowski *et al.* 1998, Gu *et al.* 1999, McMahon *et al.* 1999, Herbert 2003; Table 1). Some of the laboratory-scale experiments have closely simulated the geochemical conditions occurring within PRBs, but only within the past five years have significant numbers of mineralogical studies of cored material from field-scale operating PRBs been undertaken. Vogan *et al.* (1998) cored pilot-scale walls from two unspecified sites, one in New York and the other in Colorado, that had been operating for 24 and 18 months, respectively. At both sites, zero-valent iron is the sole reactive medium and is used to treat organic contaminants. Vogan *et al.* (1998, 1999) detected calcite, aragonite [CaCO_3], siderite [FeCO_3], green rust [simplified formula $\text{Fe}^{2+}\text{Fe}^{3+}(\text{OH})_5$], magnetite [$\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$], and unspecified Fe_2O_3 and FeOOH as secondary products. No sulfides were detected, but the probable presence of sulfate or sulfide precipitates was suspected because of declines in aqueous sulfate concentration at both sites. At Fry Canyon, Utah, a field-scale test-wall with Fe^0 filings as the reactive medium was installed to treat uranium-contaminated groundwater, and after operating from August 1997 to May 1999, precipitation of calcite and "Fe sulfide" was observed in the cores (Naftz *et al.* 2000). Cores from a pilot-scale PRB containing 100% granular iron to treat organic contaminants at a former U.S. Naval station (Moffett Field, California) were obtained after approximately 20 months of field operation. The pH within the barrier was 10 to 11, and Eh was -108 to -228 mV (Sass *et al.* 1998, Yabusaki *et al.* 2001). Corrosion coatings were reported to be predominantly hematite [$\alpha\text{-Fe}_2\text{O}_3$] and magnetite, both of which were also present in the unused iron, and minor aragonite and marcasite [FeS_2], neither of which was detected in the unused iron (Sass *et al.* 1998). Calcite with compositions ranging from near end-member to 50 at.% Fe, and ferrihydrite [nominally $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$] were identified as precipitates in a PRB at Durango, Colorado (Morrison *et al.* 2002). Cores from Fe^0 PRBs that had operated for about four years at Elizabeth City, North Carolina (treating chlorinated hydrocarbons), and at the Denver Federal Center, Lakewood, Colorado (treating Cr^{6+} and chlorinated hydrocarbons), were reported by Furukawa *et al.*

(2002) and Wilkin *et al.* (2003) to contain ferrihydrite, lepidocrocite [γ -FeOOH], goethite, magnetite, hematite, aragonite, calcite, Fe monosulfide, mackinawite, greigite, pyrite, carbonate green rust, $\text{Fe}_2\text{CO}_3(\text{OH})_2$ and siderite. Although the precipitates had reduced the pore space, neither site showed evidence of pervasive pore clogging (Wilkin *et al.* 2003).

A PRB installed in 1997 primarily for the treatment of uranium-contaminated groundwater at the Y-12 Plant site, Oak Ridge, Tennessee, has an Fe^0 zone approximately 8 m long, 0.6 m thick, and 9 m deep. After 1.2 and 2.5 years of operation of the PRB, coring showed that goethite [α -FeOOH], akaganéite [β -FeOOH], amorphous FeS, aragonite, and siderite had formed as secondary precipitates (Phillips *et al.* 2000, Gu *et al.* 2002). Significant changes observed in the cores collected after 2.5 years of operation were an increase in goethite and siderite, the detection of $\text{Fe}_2\text{CO}_3(\text{OH})_2$, lepidocrocite, calcite, and mackinawite, and confirmation of the presence of green rust (Phillips *et al.* 2003). The rates of corrosion of the filings suggested that the Fe^0 in some portions of the PRB would be consumed within less than five more years.

In summary, calcite, aragonite, siderite, $\text{Fe}_2\text{CO}_3(\text{OH})_2$, goethite, lepidocrocite, hematite, magnetite, akaganéite, ferrihydrite, green rust, marcasite, amorphous FeS, mackinawite, greigite, and pyrite have been reported for the preceding PRBs, all of which use or used Fe^0 as the reactive medium. PRBs utilizing an organic-matter-based medium (rather than Fe^0) typically treat relatively sulfate-rich effluents, and whereas several of the above-mentioned minerals are present, the precipitate assemblages formed from the sulfate-rich effluents differ considerably, as is discussed in the two case studies described below. A preliminary report on the case-study sites was given by Jambor & Mountjoy (2003).

Current studies: methods

A core for mineralogical study was obtained from the Nickel Rim site near Sudbury, Ontario, by using a wire-line rig in which the inner sleeve was 5 cm in diameter and penetrated the barrier vertically for 3.35 m. The core and sleeve were cut into easily handled lengths that were capped in the field and were stored frozen until mineralogical examination. The industrial site is near Vancouver, British Columbia, and has both a pilot-scale PRB and a subsequently installed full-scale wall. The samples from both of the Vancouver-site PRBs were obtained with a split spoon and Becker Hammer drill rig. All samples recovered from the pilot-scale PRB were wrapped in plastic and frozen on-site; those from the full-scale wall were temporarily iced, and then were laboratory-frozen on the day of collection.

The mineralogical studies for the three PRBs at the two sites were done in different years, but the same procedures were followed. All of the selected material was placed on plastic receptacles and was allowed to

dry at room temperature. Some of the samples from the British Columbia site contained drainable fluid, which was collected and allowed to evaporate at room temperature. Fluid from one of the pilot-wall samples yielded sparse crystals of gypsum, but otherwise no precipitates were observed on the samples or from the evaporated fluids; no color changes, such as would occur from the oxidation of green rust ("fougerite"; Génin *et al.* 1998, 2001), were observed in the as-received solids.

The bulk of the material in the retrieved samples contains pea gravel, for which no evidence of alteration is present. The gravel was removed by hand-picking to increase the proportion of organic-matter-rich material, but no attempt was made to remove the fines (<2 mm). The hand-picked residue was prepared as standard (26 × 46 mm) polished thin-sections; to minimize dissolution of water-soluble precipitates, if present, no water was used during section preparation.

The sections were studied by optical microscopy using both transmitted and reflected light, and many of the areas deemed to merit further study were examined by scanning electron microscopy (SEM) using a Philips XL-30 instrument with a coupled energy-dispersion analyzer (EDS); supplementary chemical compositions were obtained with a Cameca electron microprobe. Several Debye-Scherrer X-ray powder-diffraction patterns were obtained from mounts that were prepared while viewing the relevant particle under the petrographic microscope.

The iron filings used in a portion of the full-scale wall at the British Columbia site are produced from scrap metal by Connelly GPM Inc., Chicago, Illinois. According to the manufacturer's 1998 data, the filings contain 89.8 wt.% Fe^0 and 2.85 wt.% carbon; a batch of the filings was examined by Gui & Gillham (2002), who reported that particle sizes range from about 2 mm to ~300 μm , with an average surface-area of 1.80 m^2g^{-1} . A split of the specific batch of filings that was employed in the Vancouver PRB is archived at the University of Waterloo, and a portion of that sample was used for X-ray diffractometry and optical microscopy.

CASE STUDY: NICKEL RIM MINESITE

The small underground Nickel Rim mine near Sudbury, Ontario, ceased operations in 1958. Like other deposits in the Sudbury camp, Nickel Rim ore consisted largely of chalcopyrite [CuFeS_2] and pentlandite [(Fe,Ni) $_9\text{S}_8$]; on-site milling yielded about 0.9 Mt of tailings that contain 3–5 wt.% $\text{S}_{\text{sulfide}}$, nearly all of it as pyrrhotite [Fe_{1-x}S]. The tailings were deposited in an elevated impoundment, wherein oxidation of the sulfides has resulted in acidic drainage containing up to 9.8 g L^{-1} Fe, 24 g L^{-1} SO_4 , and 698 mg L^{-1} Ni (Johnson *et al.* 2000). At the western part of the impoundment, the poor-quality drainage forms a plume within a bedrock-confined sandy gravel aquifer, 3 to 8 m thick, that pinches to about 15 m width and 3.6 m depth

before discharging to a pond and adjacent lake whose near-surface pH is about 3 (Fig. 2).

Following laboratory testing of various mixtures of reactive medium (Waybrant *et al.* 1995, 1997, 1998, 2002) and the 1993 installation and subsequent monitoring of field-site test cells (Blowes *et al.* 1995a), a full-scale PRB was emplaced in 1995 (Benner *et al.* 1997, 1999). The PRB was the first of its kind in that it was designed to treat dissolved metals by using a sulfate-reduction process for remediation. The organic zone in the barrier is 15 m long, 4.3 m wide, and 3.7 m deep, within which the reactive medium does not contain Fe^0 ; rather, the medium consists of 20 vol.% each of leaf compost and a municipal compost of mixed composition, 9% wood chips, and about 1% limestone, all of which were blended with 50% pea gravel to enhance permeability and to ensure that the hydraulic conductivity of the mixture is greater than that of the inflow aquifer (Blowes *et al.* 2003). The organic zone is sandwiched between emplaced sand exteriors, each 2 m in thickness.

After one year of operation, inflow concentrations of 740–1000 mg L^{-1} Fe had decreased to $<100 \text{ mg L}^{-1}$ within the barrier. SO_4 had decreased from 2400–3800 mg L^{-1} to 110–1900 mg L^{-1} , Ni concentrations of up to 30 mg L^{-1} had declined to $<0.2 \text{ mg L}^{-1}$, and alkalinity had increased from 60–220 mg L^{-1} to 850–2700 mg L^{-1} (Blowes *et al.* 2000). The barrier ideally contains enough organic material to remove Fe and sulfate for >100 years (Benner *et al.* 1997), but declines in performance after three years of operation were observed (Benner *et al.* 2000, 2002). Although the rate of Fe removal had decreased by about 50%, more than 250 mg L^{-1} Fe and $>1000 \text{ mg L}^{-1}$ SO_4 were still being removed. Benner *et al.* (2001, 2002) suggested that the principal reasons for the temporal decrease in performance are a diminution in the availability and reactivity of the organic carbon

over time, coupled with variations in flow rates through different portions of the barrier. The distance traversed annually by groundwater flow through the barrier averages about 16 m, and average residence-time for the fluid is about 60 days in the central part of the PRB and up to 165 days in the surrounding zone (Smyth *et al.* 2001, Blowes *et al.* 2003).

The barrier was cored after two years of operation, at which time it was observed that mackinawite had precipitated on the piezometer tubing and that S accumulation in the organic material was chiefly associated with acid-volatile sulfides (AVS), which is the non-pyritic fraction as determined by chemical extraction (Herbert *et al.* 2000). In a study of more recently collected material, an increase in the AVS has also been detected in the down-gradient portion of the aquifer receiving the effluent after its passage through the barrier (Doerr *et al.* 2003).

In July 2001, after almost six years of operation, the PRB was cored for further mineralogical and geochemical studies. The material examined mineralogically is from a borehole adjacent to piezometer nest RW29, shown by Benner *et al.* (1999) and Herbert *et al.* (2000) to be within the PRB and adjacent to its inflow side, where the received contaminants should be at their highest concentrations. The pH and Eh shown in Figure 3 provide a general indication of the geochemical conditions at the cored site.

The mineralogical study revealed that precipitation of Fe within the barrier is occurring in various forms, the most common of which are sulfides (Figs. 4c, d, 5a) and Fe oxyhydroxides in a ring-type form (Fig. 5b) and in fragments with a complex-textured, commonly “swirled” form (Fig. 5a). The sulfides, most of which are present as replacements of the cells within organic matter, are less abundant than the oxyhydroxides as sinks for Fe. Framboidal pyrite has been observed, but is relatively rare. The framboids are intact, with no indications that some may have disintegrated from polyframboidal aggregates during sample preparation. None of the pyrite occurs as isolated single crystals, such as cubes. Most of the Fe sulfide in the sections, in the few instances where optically resolvable, has the appearance of greigite and pyrrhotite rather than pyrite. Where greigite and pyrite coexist, the outward succession is to peripheral pyrite (Figs. 6c, d). Where greigite–pyrrhotite and Fe oxyhydroxides coexist, the sulfide mineral forms a narrow rind; the opposite relation, *i.e.*, a rim of oxyhydroxide on the sulfide, has not been observed. Although there is undoubtedly overlap in the precipitation of the various minerals, the general progression is Fe oxyhydroxide \rightarrow greigite (or pyrrhotite) \rightarrow pyrite. The presence of early-stage mackinawite, as reported by Herbert *et al.* (2000), further suggests that greigite crystallization was preceded by that of mackinawite. Thus, the typical sequence to formation of pyrite in accordance with Reaction 5 seems to have been followed. The general paucity of pyrite and the sparse-

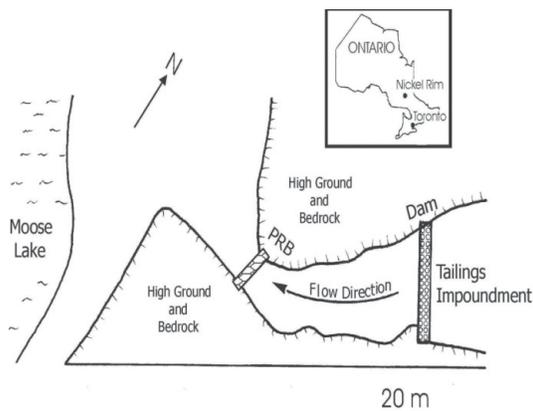


FIG. 2. General setting of the full-scale PRB at the Nickel Rim site near Sudbury, Ontario.

ness of framboids, together with the apparent relative abundance of greigite, suggest that sulfide precipitation is still at an early stage and that transformations will occur over time as H_2S continues to be generated. Other Fe minerals identified in the polished thin-sections are goethite, hematite, maghemite, and isolated grains of native iron, but all are quantitatively sparse relative to the aforementioned sinks for Fe. The identification of hematite was confirmed by a Debye-Scherrer X-ray pattern of a large area (0.5 mm) of texturally complex material resembling some of the fragmental-type Fe oxyhydroxides (Figs. 6a, b). Fragmental-type Fe oxyhydroxide is a generalized term insofar as the fragments consist predominantly of goethite, but some of the intricately intergrown layers and swirls consist of maghemite and hematite.

Rather than sorption to the Fe oxyhydroxides, dissolved Ni in the PRB has precipitated as the native metal (Figs. 4b, 6e). As well, some of the native nickel has with it an Fe-bearing Ni sulfate (Fig. 6f) and a possible Ni sulfate-phosphate, both of which are later than the native nickel.

Distinctly secondary carbonate minerals are uncommon. Some of the material included within the fragmental Fe oxyhydroxides is siderite, but other associations have not been observed. However, the optical indications are that secondary carbon has been deposited; the carbon, which occurs as irregular particles whose shapes are similar to those of the fragmental Fe-oxyhydroxides, varies optically from completely isotropic to particles whose strong anisotropy is similar to that of graphite (Figs. 5c, d). Despite the apparent crystallinity, however, both optical varieties proved to be X-ray amorphous. Carbon, both isotropic and anisotropic, that apparently formed *in situ* has also been observed at the second case-study site, described below.

The principal purpose of the installation of the Nickel Rim PRB was to decrease the content of dissolved Fe because the relevant aquifer discharges to adjacent Moose Lake (Fig. 2), whereupon oxidation of Fe^{2+} and the subsequent hydrolysis generate acidity. The PRB has not only reduced the Fe content of the plume, but the emergent water now has an excess

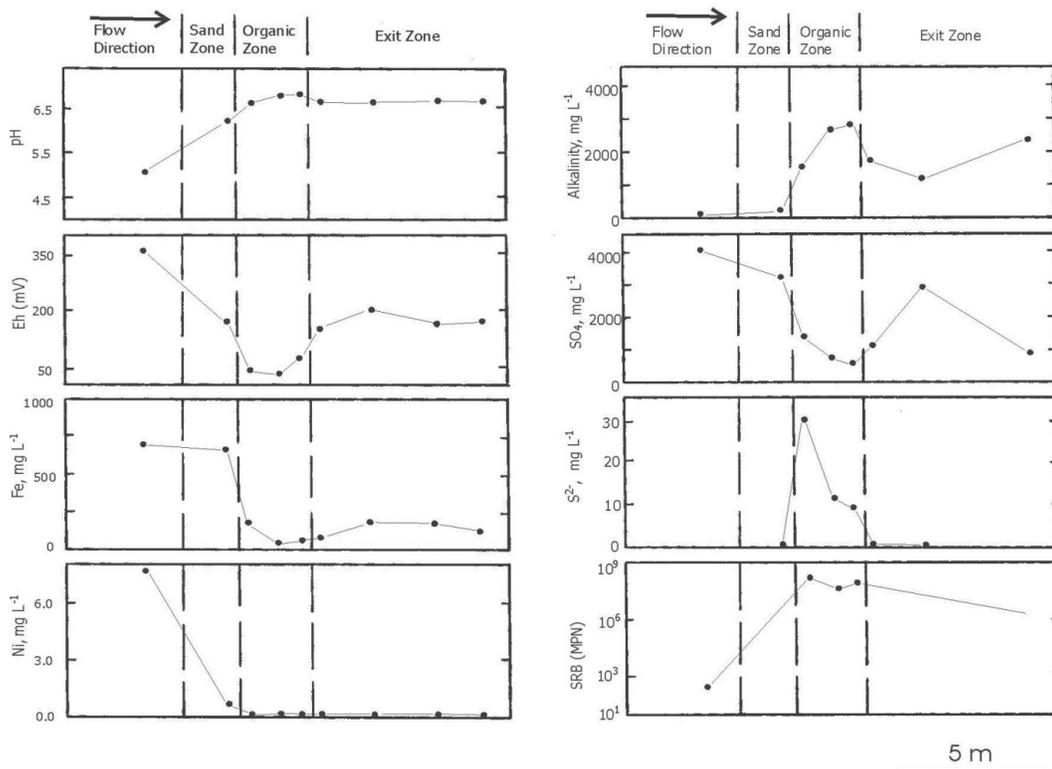


FIG. 3. Geochemical characteristics of the influent, treatment zone, and effluent at the Nickel Rim site. SRB are sulfate-reducing bacteria, MPN (Most Probable Numbers); the slope of the line within the Exit Zone is toward data points that are farther down-gradient in the sandy gravel aquifer. The Exit Zone includes 2 m of sand emplaced adjacent to the Organic Zone. Data are from Benner *et al.* (1999).

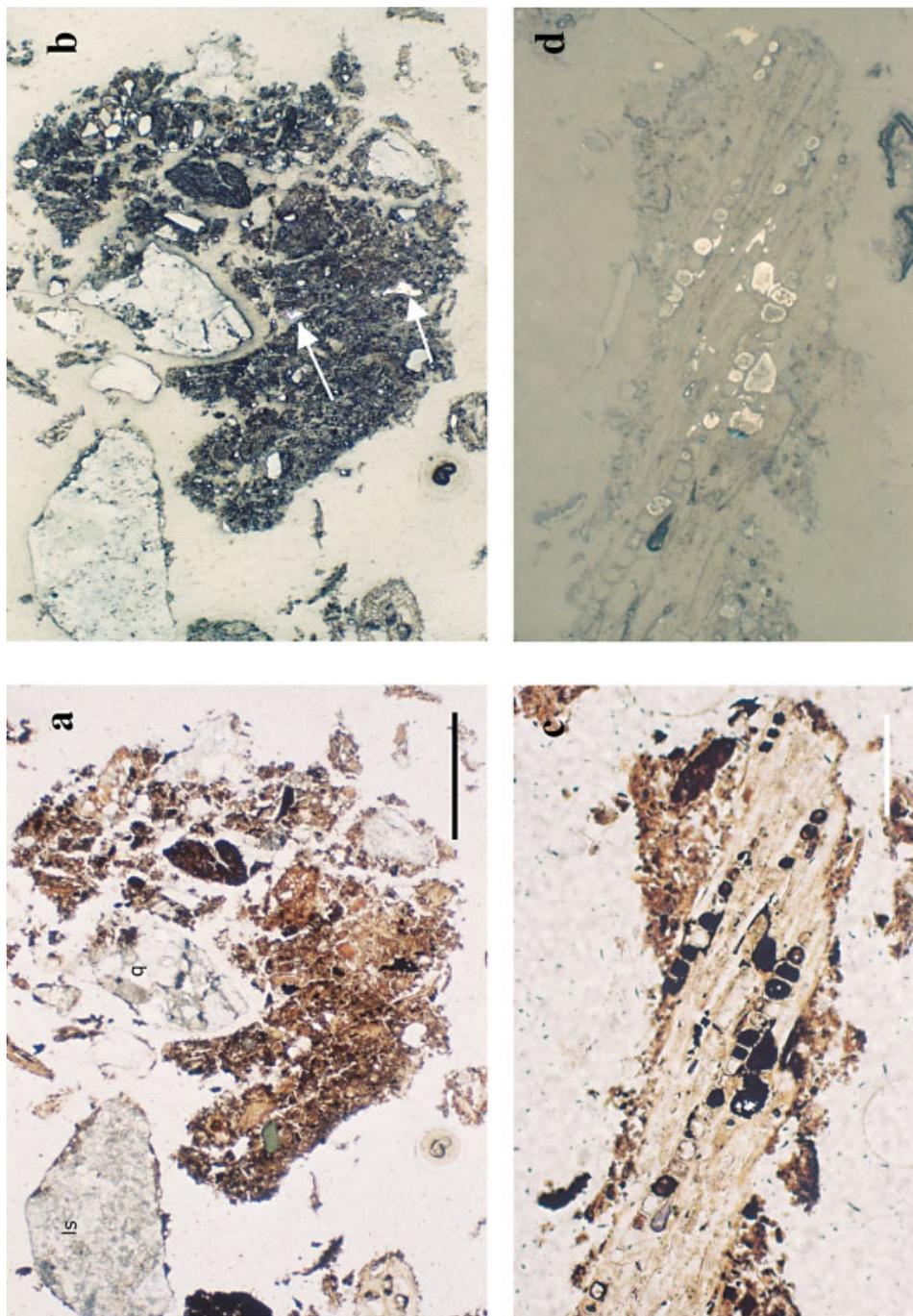


FIG. 4. Nickel Rim PRB. (a) Overview of the treatment medium, in plane-polarized transmitted light and (b) in reflected light, bar scale: 0.5 mm. The brownish material in (a) is the organic medium, ls is a fragment of limestone, and q is a fragment of pea gravel, here mainly quartz. The upper arrow in (b) points to a particle of native nickel, and the lower arrow points to a particle of carbon that is shown at higher magnification in Figure 5. (c) Transmitted light and (d) the same field in reflected light, bar scale: 100 μm , showing replacement of cellular organic matter by sulfides, which are opaque in (c) and whitish in (d). The main sulfide has the formula $\text{Fe}_{0.97}\text{S}$ and is strongly anisotropic.

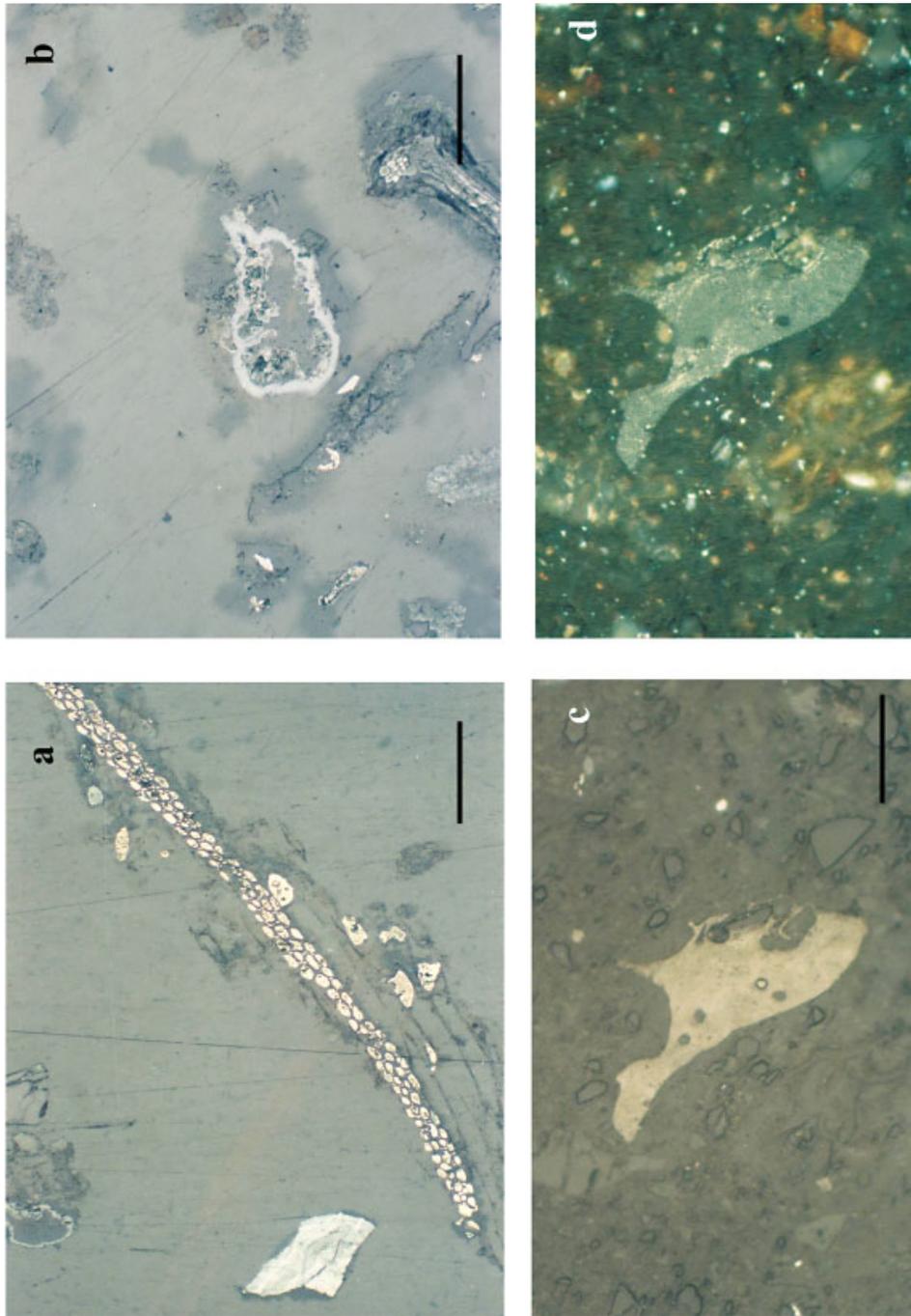


FIG. 5. Nickel Rim PRB. (a) Replacement of organic matter by Fe sulfides consisting mainly of greigite with subordinate pyrite; reflected light, bar scale: 100 μm . The whitish particle on the far left is fragmental Fe oxyhydroxide. The greigite, whose identification was confirmed by XRD, has the composition $\text{Fe}_{3.2}\text{S}_4$. (b) Ring-type Fe oxyhydroxide in reflected light, bar scale: 100 μm . The cores in this type of texture typically consist only of the mounting medium, and the Fe oxyhydroxide typically contains several percent S. (c) Reflected light and (d) the same field with polarizers crossed, bar scale: 50 μm , showing the carbon particle in Figure 4b and its strongly anisotropic, finely polycrystalline character.

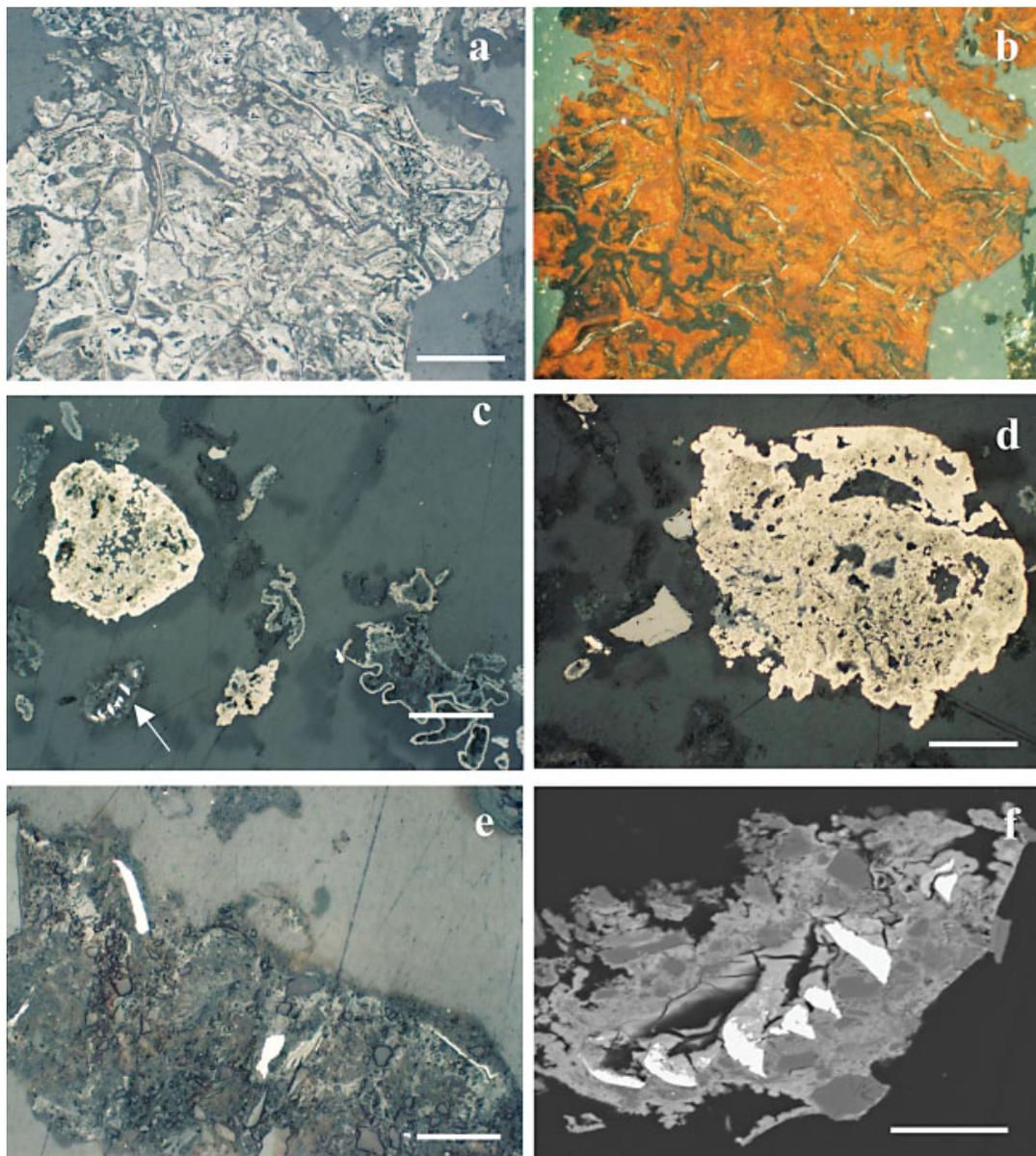


FIG. 6. Nickel Rim PRB. (a) Complex replacement texture in reflected light, and (b) the same field with polarizers almost crossed and internal-reflection mode. The reddish mineral is hematite, and the strongly anisotropic “threads” are carbon. Bar scale: 100 μm . (c) The large particle on the left is greigite rimmed by pyrite; the thin rinds on other particles are Fe oxyhydroxide with an exterior film of Fe sulfide that is probably greigite (analyzed composition $\text{Fe}_{3.2}\text{S}_4$). The arrow points to a group of white grains of native nickel. Reflected light, bar scale: 100 μm . (d) The main mass is greigite, as confirmed by X-ray powder diffraction, and the outer, yellowish rim is pyrite. The adjacent grey grains on the left are primary ilmenite. Reflected light, bar scale: 50 μm . Figures (c) and (d) show the largest particles of secondary Fe sulfide observed in the Nickel Rim samples. (e) The white grains, including the thread-like grain on the far right, are native nickel in mainly organic matter. Reflected light, bar scale: 100 μm . (f) Back-scattered-electron image of the native nickel shown in (c); bar scale: 10 μm . The nickel (white) is enclosed within a medium-grey, cracked Ni > Fe sulfate or similar compound. The slightly darker inclusions are quartz and Al-bearing silicates.

acid-neutralizing capacity, thereby helping to reduce the existing acidity within the receiving lake (Benner *et al.* 1997, Blowes *et al.* 2003).

CASE STUDY: INDUSTRIAL SITE NEAR VANCOUVER

The site is adjacent to a marine inlet, where ore concentrate is mechanically transferred from railcars and thence to ships that transport the material for further processing in other countries. The site consists predominantly of unconsolidated deltaic sands and gravels, >45 m thick, to which fill from unknown sources was periodically added to raise the ground level and extend the shoreline (McGregor *et al.* 2002). The oxidation of sulfide minerals entrained within the sediments has resulted in groundwater contamination by various dissolved heavy metals, including Cu, Zn, Cd, and Ni, whose discharge to the marine inlet has been deemed to be a potential threat to the shoreline ecosystem (Ludwig *et al.* 2000). Metal contamination is confined to the upper 15 m of the aquifer, with the highest contamination in the uppermost 6 m. Dissolved Cu at some sites on the property has exceeded 200 mg L⁻¹ (Ludwig *et al.* 2000, 2002).

A mineralogical study has shown that the sulfide sources of Cu are mainly chalcopyrite and lesser bornite [Cu₅FeS₄] that are disseminated in the unconsolidated arenaceous sediments and are also present locally as thin sulfide-dominant layers. Sphalerite [(Zn,Fe)S] is the main source of Zn and Cd; galena [PbS] and other primary sulfides, including pyrite, also are present. Although the amount of pyrite is proportionally low relative to both the total sulfide content at the site and the high content that typically prevails at sites of acid mine-drainage, concentrations of groundwater sulfate are nevertheless about 1000 mg L⁻¹ (Blowes *et al.* 2003).

In March 1997, a pilot-scale PRB, 10 m long, 2–2½ m wide, and 6–6½ m deep, was installed to intercept the path of groundwater flow. Descriptions and geochemical data given below are from McGregor *et al.* (1999, 2000) and Ludwig *et al.* (2000, 2002). Excavation of the trench for the PRB was done with a hydraulic bucket, and a slurry of biodegradable guar gum (Day *et al.* 1999) was pumped into the trench to prevent collapse of the unconsolidated-sediment walls. The reactive mixture in the PRB consists of 15 vol.% leaf compost and about 1% limestone, with 84% pea gravel (D_{50} = 8.5 mm) in the blend to ensure an appropriate permeability. Thus, like the unit at Nickel Rim, the pilot PRB at the industrial site does not contain zero-valent iron in the treatment medium.

Subsequent study of the hydraulic conductivity indicated that the influent residence-time within the barrier is about three days. The pH of the influent is slightly less than 6, and that of the effluent is only marginally higher, but influent Eh decreases from 416 mV to within-barrier values of –18 to –27 mV; accordingly, concentrations

of dissolved sulfide increase from <1.0 µg L⁻¹ to within-barrier values of about 1700 µg L⁻¹. Figure 7 shows the effect on the concentration of dissolved Cu, which decreases to <10 µg L⁻¹ in the outflow plume. Concentrations of other dissolved metals show similar patterns, with Zn decreasing from about 2400 µg L⁻¹ to <30 µg L⁻¹, and Cd and Ni decreasing from ~16 and 118 µg L⁻¹ to <3 and <10 µg L⁻¹, respectively.

Mineralogy of the pilot-scale PRB

Covellite [CuS] and mackinawite were noted as black precipitates on PVC tubing that was withdrawn from the pilot-scale PRB after 21 months of operation (McGregor *et al.* 2002). Prior to construction of the full-scale wall, additional coring of the pilot PRB was done, and filtrates on acetate filters from within the monitoring wells were also collected to obtain the mineralogical data reported herein. The filtrate and cores also contain small amounts of primary sulfides, *i.e.*, those that did not form *in situ*, whose presence was readily distinguishable by textural features. In the samples examined, the primary sulfides occur as typically isolated (single) disseminated grains whose observed decreasing order of abundance is chalcopyrite > pyrite > bornite > sphalerite >> galena >> molybdenite [MoS₂].

Minerals designated here as *secondary* are those that have precipitated within the barrier. The sulfides are dominated by framboidal pyrite (Fig. 8a) and blue-reflectance Cu sulfides that are mainly covellite. As in the Nickel Rim PRB, secondary carbon varies from optically isotropic to strongly anisotropic and occurs in fragments, some of which have indications of layering that is made evident by the incorporation of masses of minute inclusions of lithic material or former voids (Fig. 8a). Secondary chalcopyrite is common in small amounts, chiefly as rims on various non-sulfide cores (Figs. 9c, 10); locally, the rims oscil-

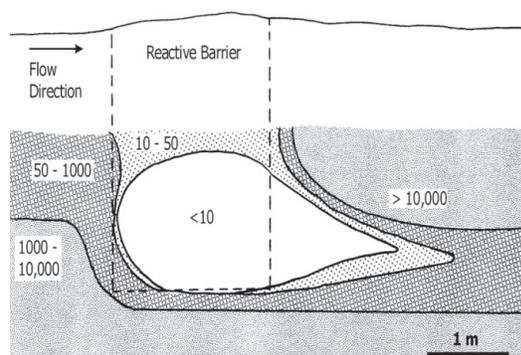


Fig. 7. Distribution of Cu (µg L⁻¹) in the Vancouver pilot-scale PRB, 21 months after installation (data from Ludwig *et al.* 2002).

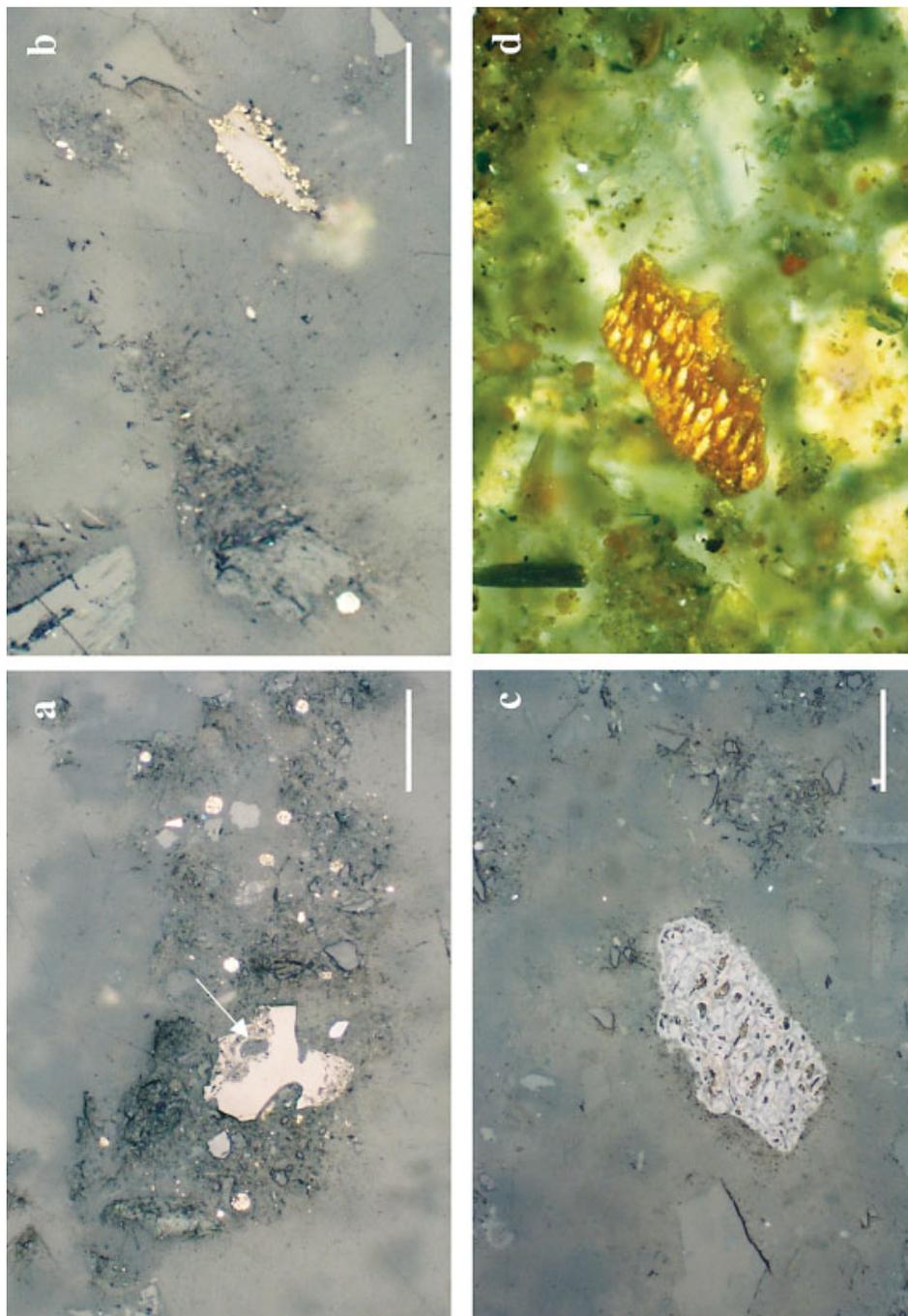


FIG. 8. Industrial site pilot-scale PRB; bar represents 100 μm . (a) Reflected light, showing a fragment of optically isotropic carbon and numerous associated circular frambooids of pyrite. The top and bottom of the carbon are riddled with inclusions, but the large grey "inclusion" at the arrow tip is a former void. (b) Reflected light, showing on the right a particle of optically isotropic carbon with attached peripheral grains of secondary chalcopyrite. (c) Reflected light and (d) the same field with internal reflection, showing Fe oxyhydroxide replacement of cellular organic matter, within which is also a micrometric bleb of native copper (not visible at this scale). The cellular material yielded a very weak X-ray pattern of goethite.

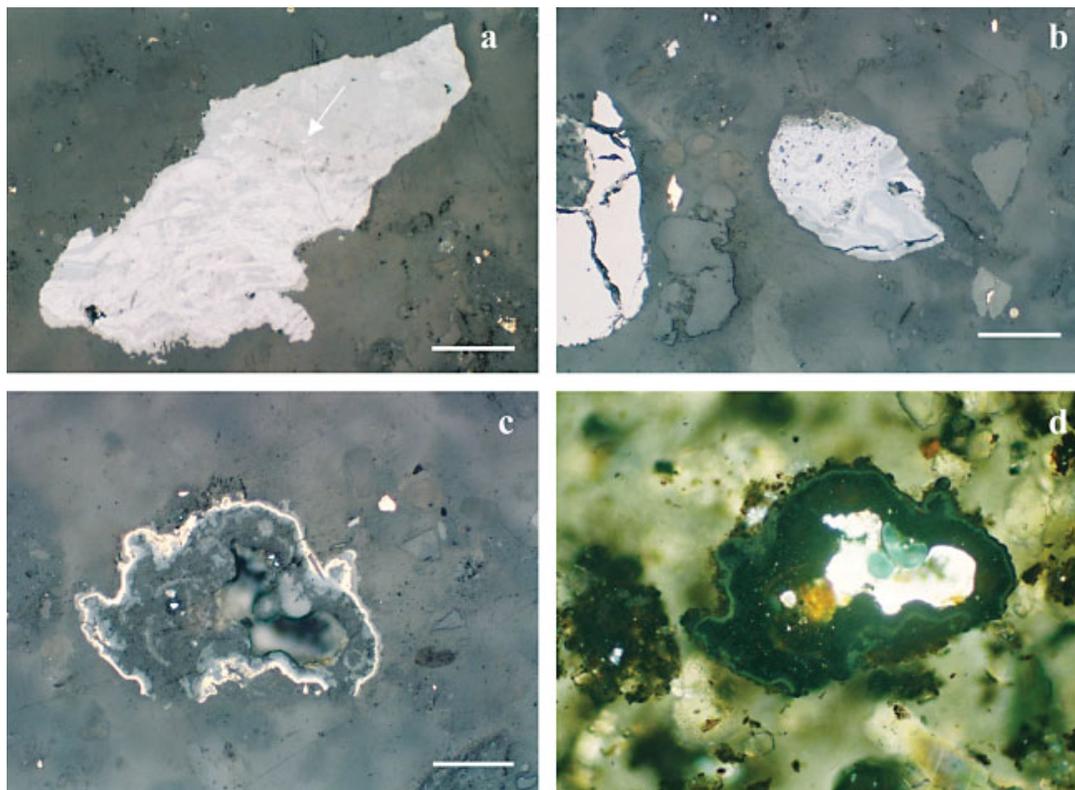


FIG. 9. Industrial site pilot-scale PRB; bar represents 100 μm ; all except (d) in reflected light. (a) Complex texture of fragmental Fe oxyhydroxide. At the tip of the arrow is a minute, white bleb of MnS. The upper half of the fragment consists predominantly of goethite, and the lower, higher-reflectance half is mainly maghemite. (b) Fragmental Fe oxyhydroxide consisting of maghemite and goethite; the yellowish grain to its left is primary chalcopyrite, and on the far left is a large grain of grey, primary magnetite. (c) Globules of malachite enclosed within a thin rind of secondary chalcopyrite. (d) Almost the same field as (c), but with internal reflection, showing the radial-fibrous, globular form of the malachite.

late between chalcopyrite and lesser amounts of bornite (Fig. 10e). One particle contains globular malachite [$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$] rimmed by a phase that may be a Fe–Cu (hydroxy)sulfate, and which in turn has an outer rind of chalcopyrite (Fig. 9c). The secondary-mineral cores upon which rinds of secondary chalcopyrite have formed have variable compositions (Table 2). For example, two cores, one of which is shown in Figure 10b, have compositions corresponding to that of spertiniite [$\text{Cu}(\text{OH})_2$], another corresponds to cuprite [Cu_2O], and yet others of similar form, including the presence of a narrow rim of chalcopyrite, have more complex compositions (Table 2). Illustrative of the mineralogical diversity of the cores is the fact that, in one particle, secondary chalcopyrite has been deposited on carbon (Figs. 8b, 11b), and several cores of primary magnetite have a rim of secondary pyrite rather than of chalcopyrite (Fig. 11a). However, most of the cores around which

secondary sulfides have formed are Fe oxyhydroxides and probable Fe–Cu hydroxysulfates.

Other minerals detected in trace amounts are native copper, a few blebs of native iron, and a bleb of MnS (alabandite) within Fe oxyhydroxide (Fig. 9a). Aside from framboidal pyrite, the principal sinks for Fe have been the fragmental-type Fe oxyhydroxides (Figs. 9a, b) and sorption-replacement of organic matter that is now distinctly Fe-rich (Fig. 8c). Some of the energy-dispersion spectra of the rudimentary Fe oxyhydroxides show the additional presence of Cu, and electron-microprobe analyses of the fragmental Fe oxyhydroxides indicate the local presence of trace amounts (<0.05 wt.%) of Cu and Ni. Debye–Scherrer X-ray patterns combined with the optical properties of the fragmental Fe oxyhydroxides indicate that the principal components are goethite and maghemite. The fragmental type of oxyhydroxides cement detrital material, but such occurrences are rare.

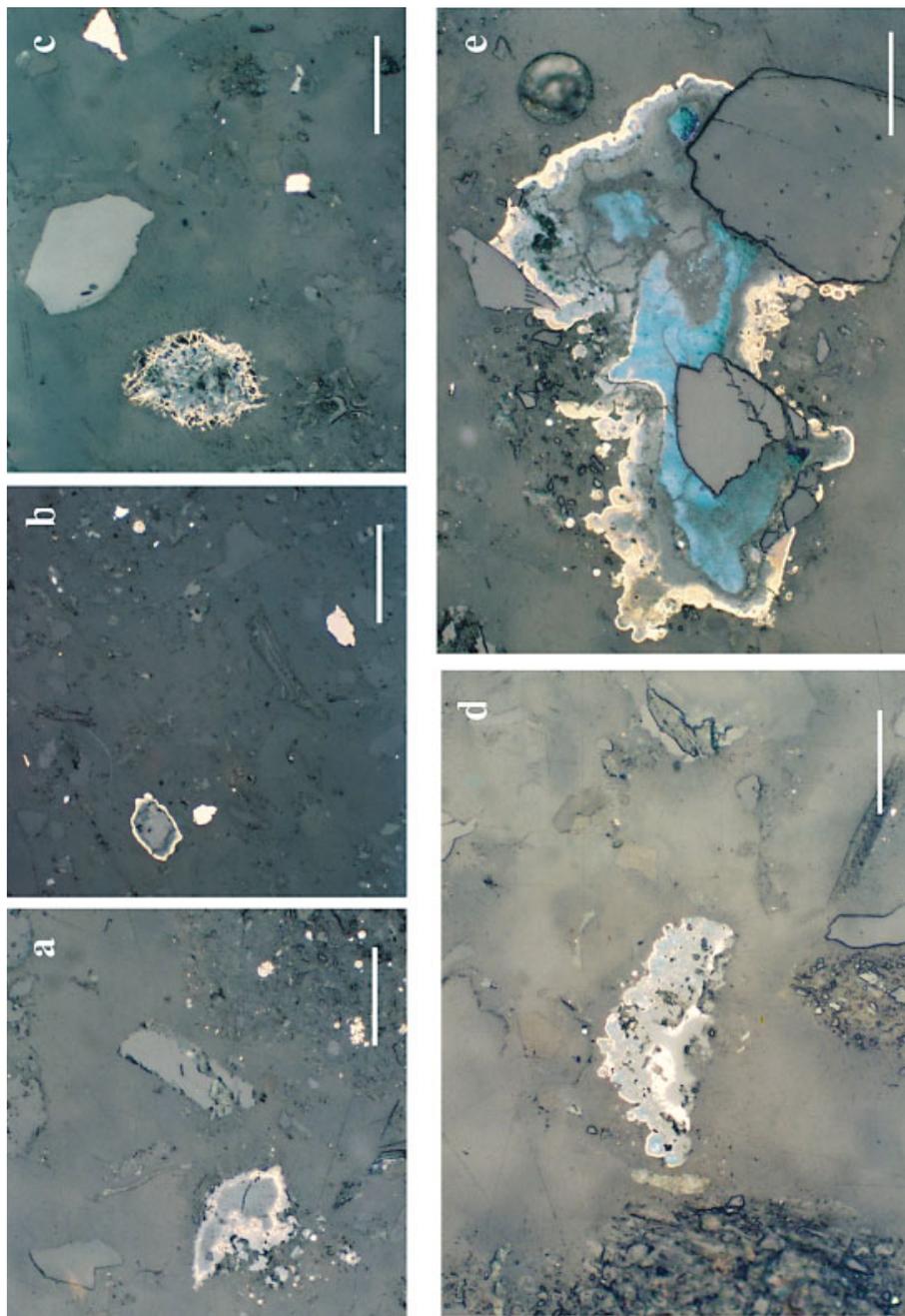


FIG. 10. Industrial site pilot-scale PRB; reflected light, bar represents 100 μm . (a) Partial rim of secondary chalcopyrite on a core of, possibly, Fe-Cu hydroxysulfate (Table 2, anal. 4). (b) Rim of secondary chalcopyrite on a core of probable spertimitite (Table 2, anal. 1) below which is a grain of primary chalcopyrite and, at the bottom right, a grain of primary bornite. (c) Fibrous secondary chalcopyrite around a core of probable Fe-Cu sulfate. Yellowish grains on the right are primary chalcopyrite. (d) Possible Cu-rich S-bearing Fe-oxyhydroxide (anal. 3, Table 2) with associated whitish secondary chalcopyrite. Near the rim of the particle is blue secondary covellite, and along the exterior is a thin rim of secondary chalcopyrite. (e) Secondary covellite (blue, confirmed by XRD) with peripheral secondary chalcopyrite and secondary brownish bornite. The chalcopyrite and bornite locally show oscillatory zoning.

McGregor *et al.* (1999) illustrated on an Eh–pH diagram that influent *versus* effluent water at the pilot PRB follows a trend primarily toward decreasing Eh, with little change in pH (6 ± 0.5). The within-barrier mineralogical trends for Cu follow a similar pattern of decreasing Eh, with early deposition of malachite and Cu and Fe–Cu hydroxides and hydroxysulfates, followed by later deposition of Cu sulfides.

Full-scale PRB

Following about four years of monitoring of the pilot-scale unit, a full-scale PRB was installed between November 2000 and March 2001 (Mountjoy & Blowes 2002). Prior to the installation, two laboratory-column tests were done using groundwater from a monitoring well near the proposed site of the full-scale barrier. One of the tests used a reactive medium whose components were like those emplaced in the pilot PRB, and the other test used a similar mixture, but with iron filings added. The iron-filings medium was observed to increase both the extent and the rate of reaction (Mountjoy & Blowes 2002).

The full-scale PRB is approximately 400 m long, 2–2½ m wide, and up to 14 m deep. During construction, more than 16 million liters of guar-gum slurry were pumped into the trench to prevent collapse of the unconsolidated sediments into the excavation (Mountjoy & Blowes 2002). The “main” wall contains a medium of compost, limestone, and pea gravel. As well, about 130 m of the eastern portion of the wall is accompanied by an additional parallel wall that was installed along the inflow side of the main wall. In this parallel section, the compost-based treatment medium was supplemented by the addition of Connelly iron filings, and this particular blend was emplaced in

the lower portion of the wall; however, the shallower portion contains only the compost-based mixture plus sand. All of the wall was covered with a geosynthetic (PVC) layer, 30 mm thick and overlain by ~0.3 m of sand, to minimize surficial infiltration from the adjacent contaminated sediments.

After several months of functioning, the full-scale PRB was cored for a mineralogical study. Like within the pilot PRB, the principal sulfide in the full wall is pyrite that occurs predominantly as individual isolated framboids rather than as polyframboidal clusters, and unlike the situation at Nickel Rim, little replacement of organic matter by sulfides has occurred. The reactive medium in the full wall also contains minute amounts of secondary marcasite, chalcopyrite, and covellite. As was observed in samples of the pilot PRB, the deposition of secondary rinds of chalcopyrite was commonly preceded by the formation of cores of Fe–Cu or Cu–Fe oxides–hydroxides. Marcasite occurs both as isolated polycrystalline particles and as aggregates of elongate to fibrous grains that enclose framboids of pyrite.

TABLE 2. CHEMICAL COMPOSITION OF SECONDARY MINERALS IN THE CORE

Grain	1	2	3	4
10a	Fig. 10b		Fig. 10d	Fig.
FeO wt. %	2.68	2.79	54.68	23.26
CuO	77.01	69.00	7.10	15.56
ZnO	1.59	3.61	0.95	0.75
SO ₂			3.35	22.07
[H ₂ O]*	18.72	24.60	31.92	
Total	100	100	100	

* By difference from 100 wt. %.

1. Corresponds to $(\text{Cu}_{0.93}\text{Fe}_{0.04}\text{Zn}_{0.02})_{21.96}(\text{OH})_{2.27}$, after deduction of 0.75 wt. % SO₂ and recalculation; ideally $\text{Cu}(\text{OH})_2$, spertinite.
2. Core similar to that shown in Figure 10b. Calculated formula, after deduction of 1.85 wt. % SO₂, is $(\text{Cu}_{20.87}\text{Fe}_{0.04}\text{Zn}_{0.04})_{29.95}(\text{OH})_{1.90} \cdot 0.42\text{H}_2\text{O}$, possibly $\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$.
3. Possibly $(\text{Fe}_{2.7}\text{Cu}_{4.1}\text{Zn}_{0.04})_{23.10}(\text{SO}_4)(\text{OH})_{14.20} \cdot 4.3\text{H}_2\text{O}$, ideally $(\text{Fe,Cu,Zn})_3(\text{SO}_4)(\text{OH}) \cdot 4\text{H}_2\text{O}$, or Fe oxyhydroxide with sorbed Cu and S.
4. Possibly $\text{Fe}(\text{Cu}_{0.22}\text{Fe}_{1.19}\text{Zn}_{0.03})_{21.93}(\text{SO}_4)(\text{OH})_{1.86} \cdot n\text{H}_2\text{O}$, simplified as $\text{FeCu}(\text{SO}_4)(\text{OH})_2 \cdot n\text{H}_2\text{O}$.

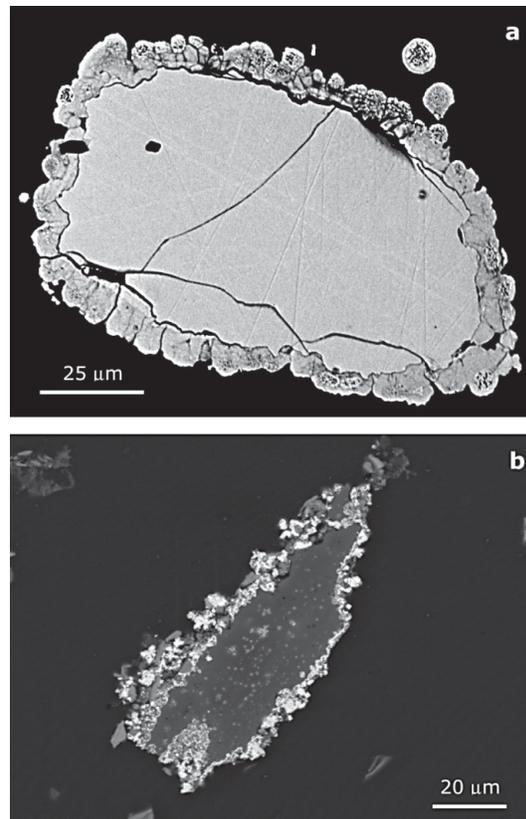


FIG. 11. Industrial site pilot-scale PRB. Back-scattered-electron images showing (a) secondary pyrite as a rim on primary magnetite, and (b) chalcopyrite on carbon, as illustrated in Figure 8b.

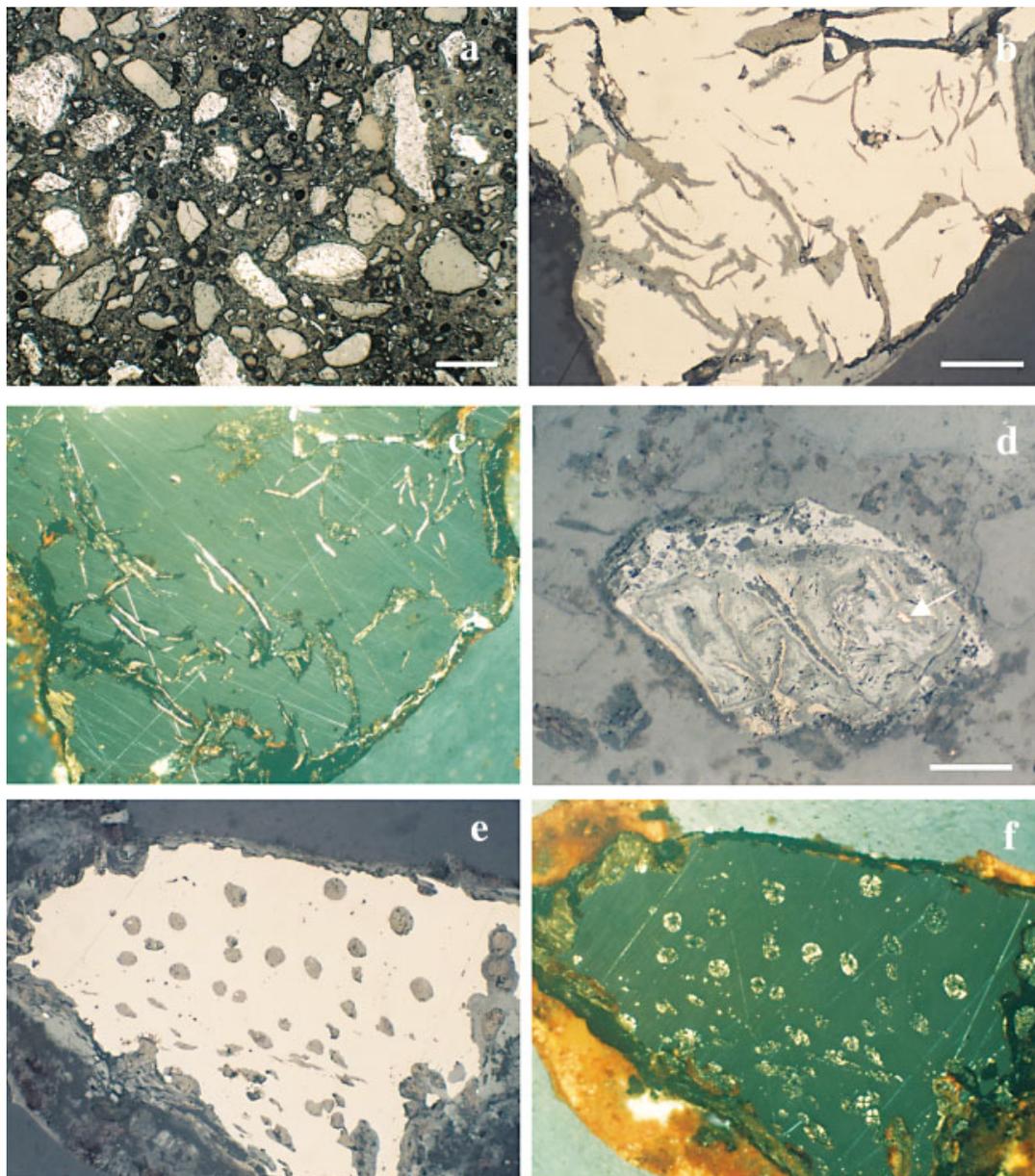


FIG. 12. Industrial site full-scale PRB. (a) Overview of the cored treatment-medium containing zero-valent iron, reflected light, bar scale 0.5 mm. The whitish particles are variably oxidized Fe^0 , and the grey particles are pea-gravel lithic fragments. (b) Initial stage of oxidation of Fe^0 , reflected light, bar scale: 100 μm . Grey Fe oxyhydroxide occurs at the rim and is also associated with veinlet-like brownish graphitic material in the interior. (c) The same field as (b), but with almost crossed polarizers. The whitish, thread-like grains are graphite, whereas most of the carbonaceous material associated with alteration is finely polycrystalline and therefore appears to have lower anisotropy. (d) Pseudomorph of compositionally and texturally complex Fe oxyhydroxide after an iron filing. Reflected light. The brownish material within the pseudomorph and along the left edge is graphite or carbon. The arrow points to a bleb of Ti metal. (e) Partly altered Fe^0 with spheroidal "primary" graphite; reflected light, bar scale: 100 μm . Penetration of Fe-oxyhydroxide alteration along graphitic centers is evident at the far right. (f) Same field as (e), but with polarizers almost crossed, showing the radial fibrous character of the graphite spheroids.

In core samples containing the Fe^0 treatment medium, the principal reaction has been partial replacement of the filings by Fe oxyhydroxides that form rims and veinlets (Fig. 12). Mineralogical examination of the archived, unreacted filings showed that, in addition to metallic iron, the filings contain graphite, magnetite, maghemite, hematite, and traces of an unidentified optically anisotropic Fe oxide. The various oxides associated with the archived Fe^0 are not uniformly distributed insofar as many of the filings either lack or have little oxide coating; only rarely do the particles consist chiefly or wholly of oxides, and the oxides invariably show an outward progression toward increased oxidation. Thus, hematite in the archived material characteristically occurs sporadically only as a thin coating and is the last oxide formed in the outward progression $\text{Fe}^0 \rightarrow$ magnetite \rightarrow maghemite \rightarrow hematite. Graphite commonly occurs as blebs that in detail have a radial fibrous structure (Fig. 12f); even more commonly, however, the graphite is present as elongate, thread-like particles that impart a reticular texture to the iron (Fig. 12c).

In the PRB-reacted filings, the exteriors of the Fe^0 particles and the sites containing graphite appear to have been the foci of initial replacement by oxyhydroxides (Fig. 12b). Where pseudomorphism of Fe^0 has occurred, some of the pseudomorphs show vestiges of the original distribution of graphite, but in other particles, the distribution of graphite is unlike that observed in the archived Fe^0 (Figs. 13a, b). Moreover, no pseudomorph containing blebs of graphite, as in Figure 12e, and none of the magnetite–maghemite intergrowths that are present in the archived Fe^0 , were observed in the reacted samples. Whether these differences are significant is an issue that requires further study to resolve. For example, the apparent non-occurrence of Fe^0 -associated magnetite is at variance with the persistence and stability of primary (detrital) magnetite and ilmenite within the PRB.

Limestone is a component of the reactive medium, but it is readily distinguishable optically from the secondary carbonates that have formed. The latter occur predominantly as a rim on lithic particles, as aggregates of varied habit, and as finely disseminated grains that may be the physically disintegrated fines of what were originally rims and clusters (Figs. 13e, 14a). Electron-microprobe analyses and Debye–Scherrer X-ray data indicate that almost all of the secondary carbonate is siderite, but aragonite also has been detected within pseudomorphs of the iron filings (Fig. 14c). Some of the peripheral Fe carbonate has a fibrous habit like that of aragonite (Roh *et al.* 2000). Electron-microprobe analysis of the siderite indicates highly variable compositions that range from almost the pure end-member to Ca- and Mn-rich (up to 6.3 wt.% CaO and 16.5 wt.% MnO). In samples containing abundant secondary carbonates, secondary sulfides are extremely sparse. Energy-dispersion analysis indicates that some of the siderite rinds are heterogeneous and locally contain Cu

oxides or hydroxides, as well as associated covellite, and it seems that some of the dissolved Zn (and abundant Mn) has been incorporated in siderite precipitates; nonetheless, at this early stage of operation of the PRB, the principal repository for solubilized Cu and Zn seems to be the Fe oxyhydroxides.

DISCUSSION

The formation of secondary Cu–Fe sulfides within the PRBs is unusual but not unprecedented for this type of geochemical setting. Copper-rich supergene environments are typically dominated by Cu–S minerals, but Cu–Fe–S minerals also form, and the co-occurrence of chalcopyrite, bornite, and native copper has been observed in a few instances (*e.g.*, Sinclair & Gasparrini 1980). In another type of setting, chalcopyrite as rims on framboidal pyrite, with associated marcasite and covellite, was described by Lett & Fletcher (1980) as an authigenic mineral in reducing, organic-matter-rich soil layers. The precipitation of covellite (Martin *et al.* 2003) and of chalcopyrite and pyrite (Pirrie *et al.* 1999) has been observed to occur under reductive conditions in organic-matter-rich muds containing mine-waste contaminants. The authigenic formation of chalcopyrite and covellite by replacement of anthropogenic Cu wire in estuarine sediments was reported by Moles *et al.* (2003), and similarly related authigenic occurrences of flocculent Zn–Fe sulfide of variable composition, and of Cu–Fe sulfide with Cu:Fe:S identical to that of chalcopyrite, have been observed in anaerobic freshwater sediments (Large *et al.* 2001). Although supergene sphalerite has only rarely been reported to occur in mineral deposits (Brown 1936, Sinclair & Gasparrini 1980), a large deposit of bacteriogenic supergene framboidal sphalerite has been identified in the Carlin Trend of Nevada (Bawden *et al.* 2003). Both sphalerite and chalcopyrite have formed as nanoscale secondary sulfides in sulfate-reducing environments in mining-contaminated anoxic sediments associated with the Clark Fork River Superfund site in Montana (Hochella *et al.* 2005). Bornite has been synthesized from aqueous solutions at room temperature (Cuthbert 1962), and chalcopyrite has been reported by McNeil & Mohr (1993) to be a common product of corrosion where natural conditions are appropriate.

Hardy & Gillham (1996) suggested that hydrophobic hydrocarbons may form during the reaction of zero-valent iron with aqueous CO_2 , but Deng *et al.* (1997) showed that carbon impurities associated with the Fe^0 were the source of the hydrocarbons. However, in sulfate-reducing PRBs, the organic medium of treatment provides a pervasive and reactive source of carbon, and there is evidence to indicate that the unprecedented formation of secondary carbon is a characteristic feature of these PRBs. The efficient decomposition of CO_2 to carbon by reaction with “cation-excess” magnetite, as contrasted with the cation deficiency of maghemite, has

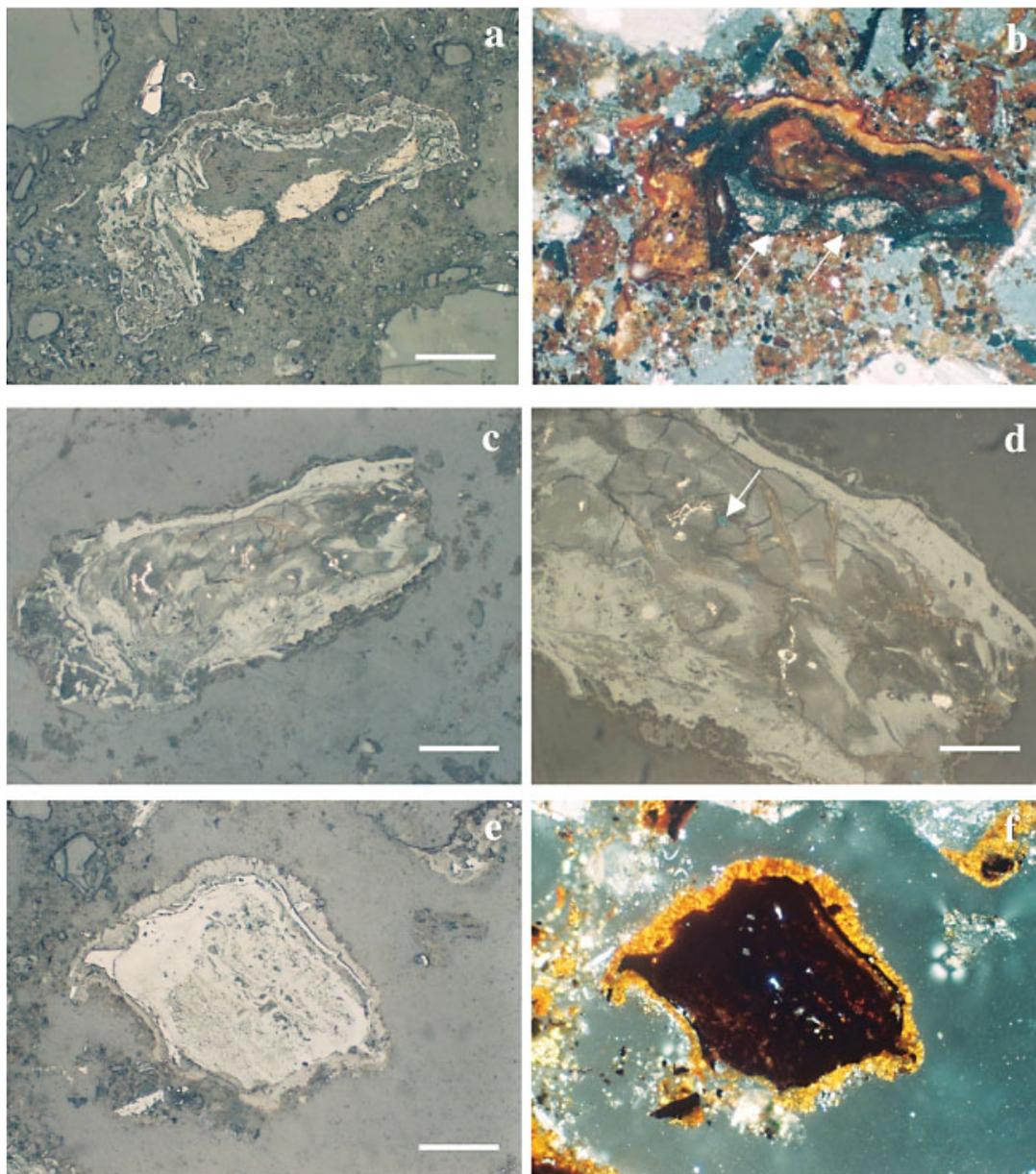


FIG. 13. Industrial site full-scale PRB; bar represents 100 μm except in (d). (a) Pseudomorph of Fe oxyhydroxide after an iron filing, showing three relatively large, lenticular particles of carbon at mid-height. (b) The same field as (a), but with polarizers almost crossed and internal reflection. Arrows point to the two largest carbon particles, which are anisotropic but finely polycrystalline. (c) Pseudomorph after an iron filing, showing the complex texture and multiple replacement-induced phases. Reflected light. (d) Enlargement of the right half of (c), reflected light, bar scale: 50 μm . The arrow points to a bleb of secondary blue covellite; to the left of the covellite is thread-like Mo metal, possibly derived from the Fe^0 . (e) Fe-oxyhydroxide pseudomorph after an iron filing, reflected light. (f) The same field as (e), but with polarizers nearly crossed, internal reflection, showing a well-developed rim of near-end-member secondary siderite that is locally Zn-rich.

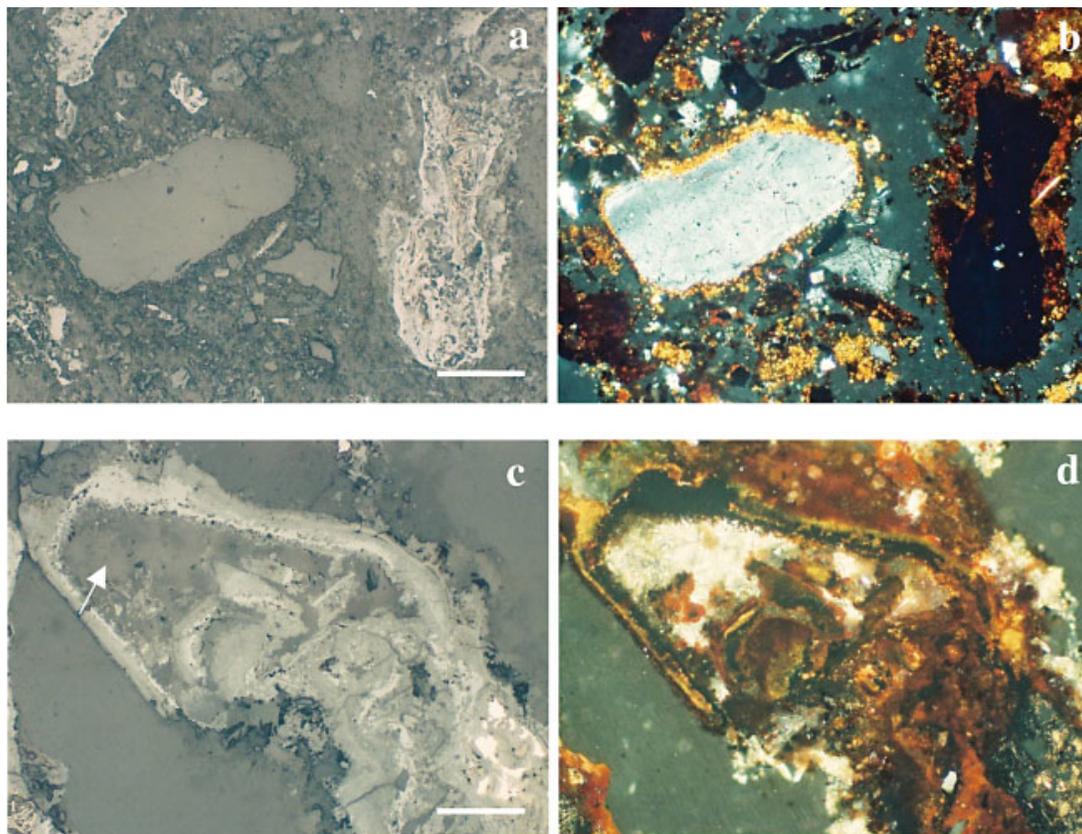


FIG. 14. Industrial site full-scale PRB; bar represents 100 μm . (a) Reflected light, and (b) with polarizers nearly crossed, internal reflection. On the right in (a) is a pseudomorph of an iron filing containing abundant brownish carbon. On the left is a large grain of albite with a rim of secondary siderite that contains ~13 wt.% MnO. (c) Part of a pseudomorph after an iron filing, in reflected light. At the bottom right are white remnants of Fe^0 with abundant associated carbon. The interior of the pseudomorph at the arrow consists of aragonite. (d) The same field as (c), but with polarizers almost crossed, internal reflection. White areas are aragonite.

been demonstrated by Tamaura & Tabata (1990), and it is possible that analogous reactions occur at ambient temperatures in PRBs. Detection of inorganic carbon is commonly interpreted to represent the carbonate-mineral fraction in PRBs, but the results may be misleading if biotic reducing conditions are present.

CONCLUSIONS

PRBs offer an effective method for the remediation of a variety of subsurface aqueous contaminants. The question of long-term effectiveness remains to be answered; although several studies have observed declines in performance over time (Mackenzie *et al.* 1999, Yabusaki *et al.* 2001, Benner *et al.* 2002, Klausen *et al.* 2003, Morrison 2003, Li *et al.* 2005), the declines are not synonymous with a lack of effectiveness. Aside from considerations about the design of PRBs

(Robertson *et al.* 2005), the principal concerns about long-term treatment generally relate to (1) decrease in porosity and permeability through the accumulation of secondary minerals (and gas; Zhang & Gillham 2005), and (2) decrease in reactivity because of the armoring effect of secondary coatings or because of the consumption of the more accessible portions of the reactive medium, especially the organic carbon.

At the British Columbia site, consumption of the Fe^0 has been extensive over a short period, but the rapid oxidation may be related to the initiation period, in which “fresh” Fe^0 surfaces are at a maximum, rather than reflecting steady-state, long-term conditions. The PRB will be monitored to evaluate performance and trends over time.

The cost of PRBs varies with site conditions, but an indication of the order of magnitude is that the total cost of the Nickel Rim barrier was about \$35,000 US,

about half for the purchase and delivery of materials, and the remainder for installation (Smyth *et al.* 2001, Blowes *et al.* 2003). The industrial-site pilot PRB cost slightly less, but unit costs were similar at about \$190 US per cubic meter (McGregor *et al.* 2002). Thus, PRBs potentially represent a highly cost-effective method for remediation of a wide variety of contaminated sites.

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